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## EUROPEAN PATENT APPLICATION

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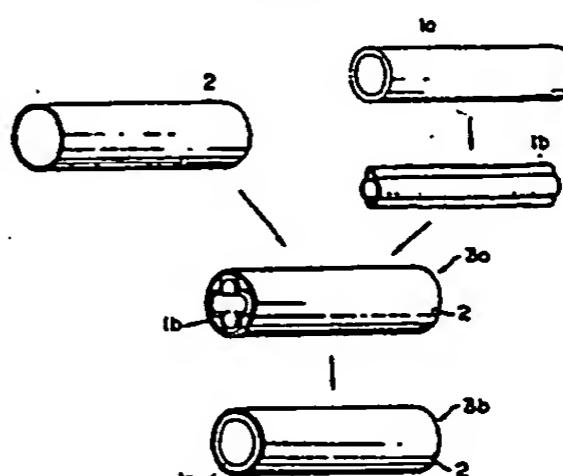
### ⑯ Shape memory hollow body and method of working the same.

⑰ A shape memory hollow body which is molded from a polyurethane elastomer produced by prepolymer process from a raw material composed of a difunctional diisocyanate, difunctional polyol, and difunctional chain extender containing active hydrogen in a molar ratio of 2.00-1.10 : 1.00 : 1.00-0.10, said polyurethane elastomer containing NCO groups and OH groups in almost equal amounts at the terminals of the polymer chains and having a glass transition point in the range of -50 to 60 °C and a crystallinity of 3 to 50 wt%, said hollow body remembering its asmolded basic shape but taking on a deformed shape which is given when it is deformed at a temperature higher than the glass transition point of the polymer and lower than the molding temperature and then set when it is cooled in the deformed state to a temperature lower than the glass transition point.

A method of working the above-mentioned shape memory hollow body (1a) remembering its basic shape, said method prising the steps of de-

forming the hollow body (1a) at a temperature higher than the glass transition point and lower than the molding temperature and then cooling it in the deformed state to a temperature lower than the glass transition point, thereby setting it in the deformed state, combining the deformed hollow body (1b) with another member, (2), and heating the combination (3a) to a temperature higher than the glass transition point, thereby causing it to restore its basic shape and achieving firm bonding of the hollow body (1a) to the member.

FIG. 1



## SHAPE MEMORY HOLLOW BODY AND METHOD OF WORKING THE SAME

The present invention relates to a hollow body molded from a thermoplastic polyurethane elastomer having the shape memory function and also to a method of working the same.

Polyurethane having a glass transition point as low as about -40°C exhibits a low modulus even at low temperatures and hence can be used in the application areas for ordinary natural rubber and synthetic rubber. On the other hand, polyurethane having a glass transition point as high as about 100-110°C exhibits a high modulus and good abrasion resistance even at high temperatures and hence finds use as a raw material for artificial wood. ("Glass transition point" will be referred to as Tg hereinafter.)

Meanwhile, the present inventors have proposed a shape memory polyurethane elastomer (in Japanese Patent Laid-open No. 293214-1986). It provides a molding which takes on an as-molded shape and deformed shape when it is heated or cooled to a proper temperature. In other words, the molding takes on a deformed shape when it is deformed at a temperature lower than the molding temperature and then cooled to a temperature below Tg while being kept deformed, so that the deformation is set. The deformed molding restores its original shape when it is heated to a temperature higher than Tg and lower than the molding temperature.

The reference cited above discloses two kinds of shape memory polyurethane elastomers. One is composed of an isophorone-based isocyanate, a polyol, and an adduct of trimethylol propane with tolylene diisocyanate (as a chain extender). The other is composed of 2,4-tolylene diisocyanate, a polyol, and 1,4-butanediol (as a chain extender).

These polyurethane elastomers contain a large amount of excess NCO groups at the terminals of the polymer molecules so that they exhibit rubber elasticity at a temperature higher than the Tg. In addition, the first one has crosslinkage formed by a trifunctional chain extender. Polyurethane elastomers having crosslinkage resemble a thermosetting polymer and hence are limited in the freedom of fabrication. That is, they are very difficult to process by injection molding, extrusion molding, blow molding, or the like.

It is an object of the present invention to provide a hollow body molded from a shape memory polyurethane elastomer which is thermoplastic and capable of melt molding (such as injection molding and extrusion molding) and exhibits rubber elasticity at temperatures higher than its Tg approximate to room temperature. It is another object of the present invention to provide a method of work-

ing said hollow body.

The first aspect of the present invention resides in a shape memory hollow body which is molded from a polyurethane elastomer produced by prepolymer process from a raw material composed of a difunctional diisocyanate, difunctional polyol, and difunctional chain extender containing active hydrogen in a molar ratio of 2.00-1.10 : 1.00 : 1.00-0.10, said polyurethane elastomer containing NCO groups and OH groups in almost equal amounts at the terminals of the polymer chains and having a glass transition point in the range of -50 to 60°C and a crystallinity of 3 to 50 wt%, said hollow body remembering its as-molded basic shape but taking on a deformed shape which is given when it is deformed at a temperature higher than the glass transition point of the polymer and lower than the molding temperature and then set when it is cooled in the deformed state to a temperature lower than the glass transition point.

The second aspect of the present invention resides in a method of working the above-mentioned shape memory hollow body remembering its basic shape, said method comprising the steps of deforming the hollow body at a temperature higher than the glass transition point and lower than the molding temperature and then cooling it in the deformed state to a temperature lower than the glass transition point, thereby setting it in the deformed state, combining the deformed hollow body with another member, and heating the combination to a temperature higher than the glass transition point, thereby causing it to restore its basic shape and achieving firm bonding of the hollow body to the member.

Fig. 1 is a schematic drawing showing the steps of fitting an inner pipe of shape memory polyurethane elastomer into a pipe.

Fig. 2 is a sectional view showing the joining of a shape memory hollow body to a pipe.

The conventional shape memory polyurethane elastomer molding depends on rigid allophanate linkages for its rubber elasticity at a temperature higher than its Tg. The allophanate linkages result from the intermolecular crosslinking which takes place when excess terminal NCO groups react with urethane linkages. By contrast, the shape memory polyurethane elastomer in the present invention is a thermoplastic chain polymer which is composed of a difunctional isocyanate, polyol, and chain extender according to a specific formulation but contains no excess terminal NCO groups. It is characterized by a specific crystallinity, a Tg approximate to room temperature, and a specific ratio of moduli measured at temperatures above and below

the Tg. This polyurethane elastomer has the partial crystallization instead of the intermolecular crosslinking. Therefore, it is a thermoplastic polymer of chain structure; nevertheless, it exhibits rubber elasticity at a temperature higher than its Tg and takes on the as-molded shape and deformed shape at temperatures above and below its Tg. In other words, it has the shape memory function. This thermoplastic polyurethane elastomer can be easily molded into a hollow body by melt molding such as injection molding and extrusion molding.

The thermoplastic polyurethane elastomer in the present invention should preferably have a crystallinity in the range of 3 to 50 wt%. With a crystallinity lower than 3 wt%, the polymer will have a low rubber elasticity at a temperature higher than its Tg. Conversely, with a crystallinity higher than 50 wt%, the polymer will have a high rubber elasticity at a temperature higher than its Tg, with the result that the ratio of moduli at temperatures 10 °C above and below its Tg is smaller.

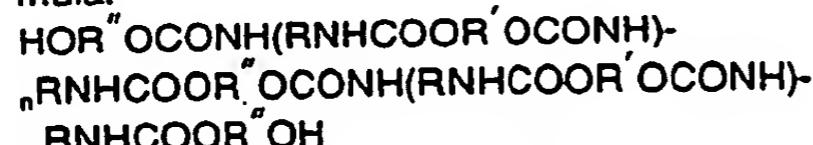
The polyurethane polymer in the present invention is produced from the following raw materials, which are illustrative only and not limitative.

The first raw material is a difunctional isocyanate which is represented by the general formula OCN-R-NCO, where R is a group having no or one or two benzene rings. It includes, for example, 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, carbodiimide-modified 4,4'-diphenylmethane diisocyanate, and hexamethylene diisocyanate.

The second raw material is a difunctional polyol which is represented by the general formula OH-R'-OH, where R' is a group having no or one or two benzene rings. The second raw material may also be a reaction product of said difunctional polyol and a difunctional carboxylic acid or cyclic ether. It includes, for example, polypropylene glycol, 1,4-butane glycol adipate, polytetramethylene glycol, polyethylene glycol, and an adduct of bisphenol-A with propylene oxide.

The third raw material is a difunctional chain extender containing active hydrogen which is represented by the general formula OH-R''-OH, where R'' is a  $(CH_2)_n$  group or a group having no or one or two benzene rings. It includes, for example, ethylene glycol, 1,4-butane glycol, bis(2-hydroxyethyl)hydroquinone, an adduct of bisphenol-A with ethylene oxide, and an adduct of bisphenol-A with propylene oxide.

The thus produced polyurethane elastomer may be represented by the following general formula.



where m is 1-16 and n is 0-16.

The following illustrates the production of the shape memory polyurethane elastomer. First, a prepolymer is prepared by reacting, in the absence of catalyst, an isocyanate component and a polyol component in the ratio shown in Table 1. To the prepolymer is added a chain extender in the ratio shown in Table 1. The resulting mixture is heat-cured to give the shape memory polyurethane elastomer, which has the basic physical properties as shown in Table 1.

In Table 1, Tg represents the glass transition point (°C) and E:E' represents the ratio of the tensile modulus at a temperature 10 °C lower than the Tg to the tensile modulus at a temperature 10 °C higher than the Tg. The crystallinity (wt%) was measured by X-ray diffractometry.

The hollow body pertaining to the present invention is made of the above-mentioned shape memory polyurethane elastomer. It remembers its basic shape when it is molded. It is given its second shape (deformed shape) when it is deformed at a temperature higher than its Tg and lower than its molding temperature and then cooled in the deformed state to a temperature lower than its Tg. Subsequently, the deformed hollow body is combined with another member, and the combination is heated to a temperature higher than its Tg, so that the hollow body restores its basic shape, firmly joining itself to the member.

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Table 1

Raw materials and molar ratio		M.W.	1	2	3	4	5	6	7	8	9	10
<b>Diisocyanate</b>												
2,4-toluene diisocyanate		174	1.5			1.5						
4,4'-diphenylmethane diisocyanate		250				1.5						
4,4'-diphenylmethane diisocyanate (carbodiimide-modified)		290				1.5						
ditto												
hexamethylene diisocyanate		303	1.5	1.5								
ditto		168										
<b>Polyol</b>												
polypropylene glycol		400										
ditto		700										
ditto		1000										
1,4-butaneglycol adipate		600										
ditto		1000										
ditto		2000										
polytetramethylene glycol		650										
ditto		850										
ditto		1000										
polyethylene glycol		600										
bisphenol-A + propylene oxide		800	1.0									
Chain extender												
ethylene glycol		62										
1,4-butaneglycol		90	0.51									
bis(2-hydroxyethyl)hydroquinone		198										
bisphenol-A + ethylene oxide		327										
ditto		360	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51	
bisphenol-A + propylene oxide		360										
<b>Measured values of physical properties</b>												
Tg (°C)		24	-10	15	-11	14	16	-45	9	6	12	
E/E'		170	73	69	23	129	133	20	117	128	97	
Crystallinity (wt%)		20	20	30				25				

Table 1 (continued)

Raw materials and molar ratio	M.W.	11	12	13	14	15	16	17	18	19	20
<b>Diisocyanate</b>											
2,4-toluene diisocyanate	174										
4,4'-diphenylmethane diisocyanate	250	1.5	1.5	1.5	1.2	1.8	1.35	1.35	1.35	1.35	1.35
4,4'-diphenylmethane diisocyanate (carbodiimide-modified)	290										
ditto	303										
hexamethylene diisocyanate	168										
<b>Polyol</b>											
polypropylene glycol	400										
ditto	700	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
ditto	1000										
1,4-butaneglycol adipate	600										
ditto	1000										
ditto	2000										
polytetramethylene glycol	650										
ditto	850										
ditto	1000										
polyethylene glycol	600										
bisphenol-A + propylene oxide	800										
<b>Chain extender</b>											
ethylene glycol	62										
1,4-butaneglycol	90										
bis(2-hydroxyethyl)hydroquinone	198		0.51								
bisphenol-A + ethylene oxide	327	0.51		0.21	0.81	0.36	0.36	0.36	0.36	0.36	0.36
ditto	360										
bisphenol-A + propylene oxide	360										
<b>Measured values of physical properties</b>											
Tg (°C)		16	-7	-6	-4	25	5	-22	10	-18	-45
E/E'		111	49	12	105	55	37	81	100	29	30
Crystallinity (wt%)		20	30	20	25	20	25	25	25	25	25

Table 1 (continued)

Raw materials and molar ratio	M.W.	21	22	23	24	25	26	27	28	29	30
<b>Diisocyanate</b>											
2,4-toluene diisocyanate	174										
4,4'-diphenylmethane diisocyanate	250	1.35	1.35	1.35	1.5	1.5	1.35				
4,4'-diphenylmethane diisocyanate (carbodiimide-modified)	290										
ditto	303										
hexamethylene diisocyanate	168							1.0			
<b>Polyol</b>											
polypropylene glycol	400										
ditto	700						1.0	1.0			
ditto	1000										
1,4-butaneglycol adipate	600										
ditto	1000										
ditto	2000										
polytetramethylene glycol	650	1.0									
ditto	1000		1.0								
ditto	600										
<b>polyethylene glycol</b>	800							1.0	1.0	1.0	1.0
bisphenol-A + propylene oxide	62										
ethylene glycol	90										
<b>Chain extender</b>											
1,4-butaneglycol	198										
bis(2-hydroxyethyl)hydroquinone	327	0.36	0.36	0.43	0.35	0.36	0.51	0.41	0.31	0.21	
bisphenol-A + ethylene oxide	360										
ditto	360										
<b>bisphenol-A + propylene oxide</b>	360										
<b>Measured values of physical properties</b>	Tg (°C)	-18	-30	-38	5	8	23	26	21	19	19
	E/E'	33	18	40	33	100	126	140	125	108	101
	Crystallinity (wt%)	25	25	25	15	15	10	15	15	15	15

Table 1 (continued)

Raw materials and molar ratio	M.W.	31	32	33	34	35	36	37	38	39	40
<b>Diisocyanate</b>											
2,4-toluene diisocyanate	174					1.5					
4,4'-diphenylmethane diisocyanate	250	1.59	1.68		1.3	1.7	1.59	1.68	1.5	1.5	1.81
4,4'-diphenylmethane diisocyanate (carbodiimide-modified)	290										
ditto	303										
hexamethylene diisocyanate	168										
<b>Polyol</b>											
polypropylene glycol	400										
ditto	700	1.0	1.0			1.0	1.0	1.0	1.0	1.0	
ditto	1000										
1,4-butaneglycol adipate	600										
ditto	1000										
ditto	2000										
poly(ether)ethylene glycol	650										
ditto	850										
ditto	1000										
polyethylene glycol	600										
bis phenol-A + propylene oxide	800			1.0					1.0	1.0	1.0
<b>Chain extender</b>											
ethylene glycol	62				0.31	0.71	0.51	0.51		0.51	0.81
1,4-butaneglycol	80				0.51						
bis(2-hydroxyethyl)hydroquinone	198										
bisphenol-A + ethylene oxide	327										
ditto	360	0.51	0.51								
bisphenol-A + propylene oxide	360										
<b>Measured values of physical properties</b>											
	Tg (°C)	10	11	22	2	15	11	12	35	40	48
	E/E'	126	126	107	83	122	100	135	124	138	152
	Crystallinity (wt%)	15	20	15	20	15	15	10	10	5	5

## EXAMPLES

The invention will be described in more detail with reference to the following examples, which are not intended to restrict the scope of the invention.

## Example 1

In this example, a hollow body (inner pipe) made of the shape memory polyurethane elastomer was fitted into an outer pipe according to the following procedure.

First, a polymer having a Tg of 48°C was prepared by prepolymer process according to the formulation of sample No. 40 shown in Table 1. The polymer was made into a cylindrical hollow body 1a having an outside diameter of 10.4 cm and a wall thickness of 5 mm by extrusion molding.

This cylindrical hollow body 1a was heated to about 65°C and then collapsed by pressing. It was cooled to about 40°C in the collapsed state so that it was set deformed. Thus there was obtained a collapsed hollow body 1b.

The collapsed hollow body 1b was inserted into a steel pipe 2 having an inside diameter of 10 cm. (The resulting combination is indicated by 3a.)

The collapsed hollow body 1b inserted into the steel pipe 3a was heated by blowing hot air (about 65°C), so that it restored its original cylindrical shape. Thus there was obtained a composite pipe 3b composed of a steel pipe 2 and a cylindrical hollow body 1a of polyurethane elastomer which was firmly bonded to the inside of the steel pipe.

This example shows that the use of the shape memory function overcomes the difficulty which was encountered in the past when the inside of a small steel pipe was coated with a polyurethane elastomer.

## Example 2

In this example, a pipe made of the shape memory polyurethane elastomer was joined to another pipe as shown in Fig. 2.

A polymer having a Tg of 40°C was prepared by prepolymer process according to the formulation of sample No. 39 shown in Table 1. The polymer was molded into a straight pipe (not shown) having an outside diameter of 5 cm and a wall thickness of 3 mm. This straight pipe remembers its as-molded shape. The end 4 (3 cm long) of the pipe was heated to about 60°C and then contracted until the outside diameter was 4 cm.

The pipe was cooled to about 35°C, with the end contracted, so that the contracted shape was set. Thus there was obtained a pipe 5 as shown in Fig. 2.

5 The end 4 of the pipe 5 was inserted into a pipe 6 having an inside diameter of 4.5 cm. When they are heated to about 60°C, the end of the pipe 5 restored its original shape, joining itself firmly to the inside of the pipe 6. The above-mentioned 10 joining procedure may be applied to joining an elbow made of shape memory polymer to a steel pipe.

15 As the above-mentioned examples show, the thermoplastic polyurethane elastomer having the shape memory function can be molded into a hollow body of any shape by melt molding such as injection molding, extrusion molding, and blowing molding.

20 In addition, the shape memory hollow body of the present invention remembers its basic shape, takes on its second shape (e.g., reduced or enlarged diameter, and bending), and restores its basic shape after it has been combined with another member. This property makes it possible to 25 join the hollow body firmly to another member.

## Claims

30 1. A shape memory hollow body which is molded from a polyurethane elastomer produced by prepolymer process from a raw material composed of a difunctional diisocyanate, difunctional polyol, and difunctional chain extender containing active 35 hydrogen in a molar ratio of 2.00-1.10 : 1.00 : 1.00-0.10, said polyurethane elastomer containing NCO groups and OH groups in almost equal amounts at the terminals of the polymer chains and having a glass transition point in the range of -50 to 60°C and a crystallinity of 3 to 50 wt%, said hollow body remembering its as-molded basic shape but taking on a deformed shape which is given when it is deformed at a temperature higher than the glass transition point of the polymer and lower than the molding temperature and then set when it is cooled in the deformed state to a temperature lower than the glass transition point.

40 2. The shape memory hollow body as claimed in Claim 1, wherein the difunctional diisocyanate is one which is represented by the general formula OCN-R-NCO, where R is a group having no or one or two benzene rings.

45 3. The shape memory hollow body as claimed in Claim 1, wherein the difunctional polyol is one which is represented by the general formula OH-R'-OH, where R' is a group having no or one or two benzene rings.

4. The shape memory hollow body as claimed in Claim 1, wherein the difunctional chain extender containing active hydrogen which is represented by the general formula OH-R'-OH, where R' is a  $(\text{CH}_2)_n$  group or a group having no or one or two benzene rings. 5

5. The shape memory hollow body as claimed in Claim 1, wherein the polyurethane elastomer polymerized by prepolymer process is one which is represented by the general formula below: 10  
HOR''OCONH(RNHCOR' OCONH)-  
 $n$ RNHCOR''OCONH(RNHCOR' OCONH)-  
 $m$ RNHCOR''OH  
where m is 1-16 and n is 0-16.

6. A method of working the shape memory hollow body remembering its basic shape as claimed in Claim 1, said method comprising the steps of deforming the hollow body at a temperature higher than the glass transition point and lower than the molding temperature and then cooling it in the deformed state to a temperature lower than the glass transition point, thereby setting it in the deformed state, combining the deformed hollow body with another member, and heating the combination to a temperature higher than the glass transition point, thereby causing it to restore its basic shape and achieving firm bonding of the hollow body to the member. 15  
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FIG. 1

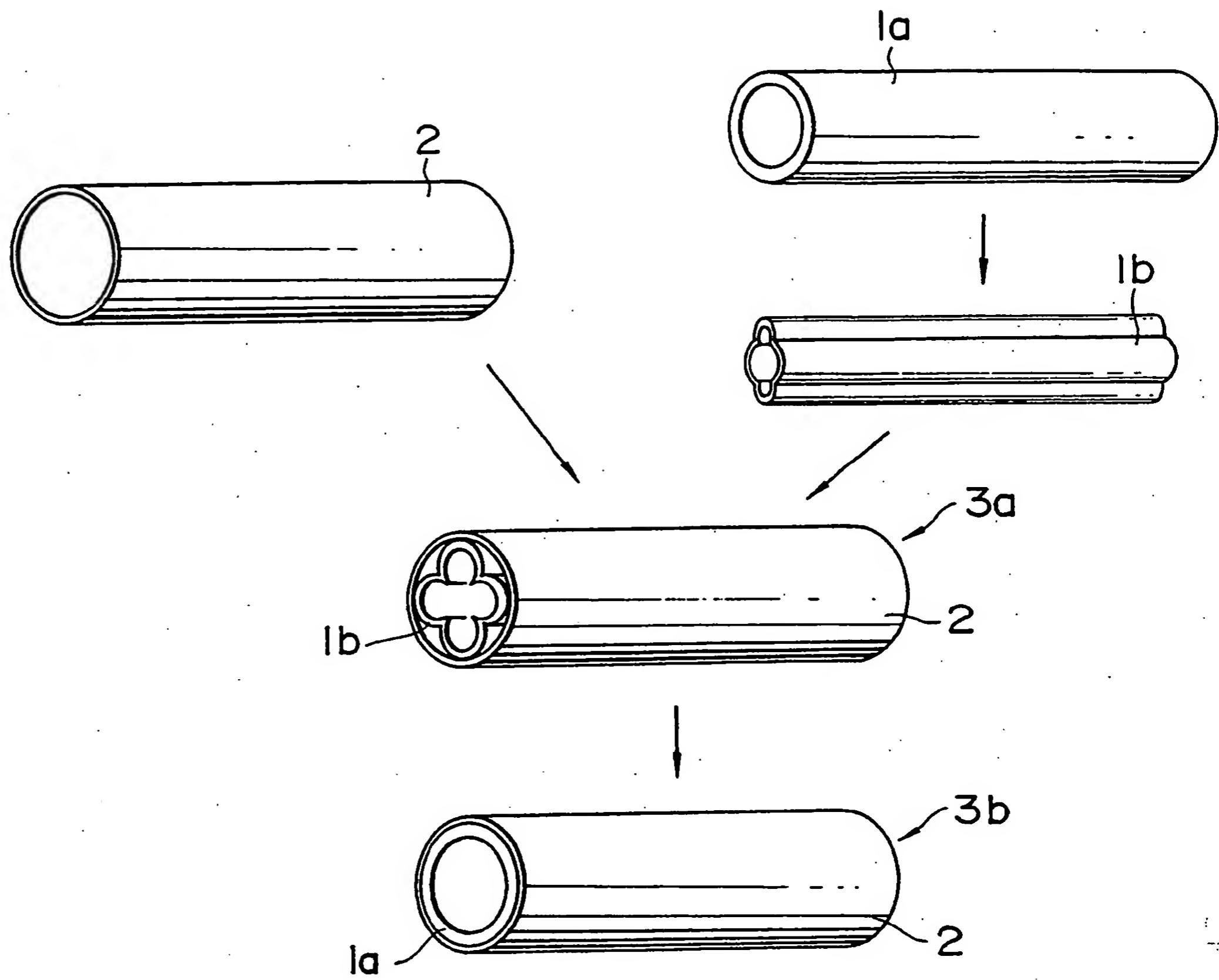
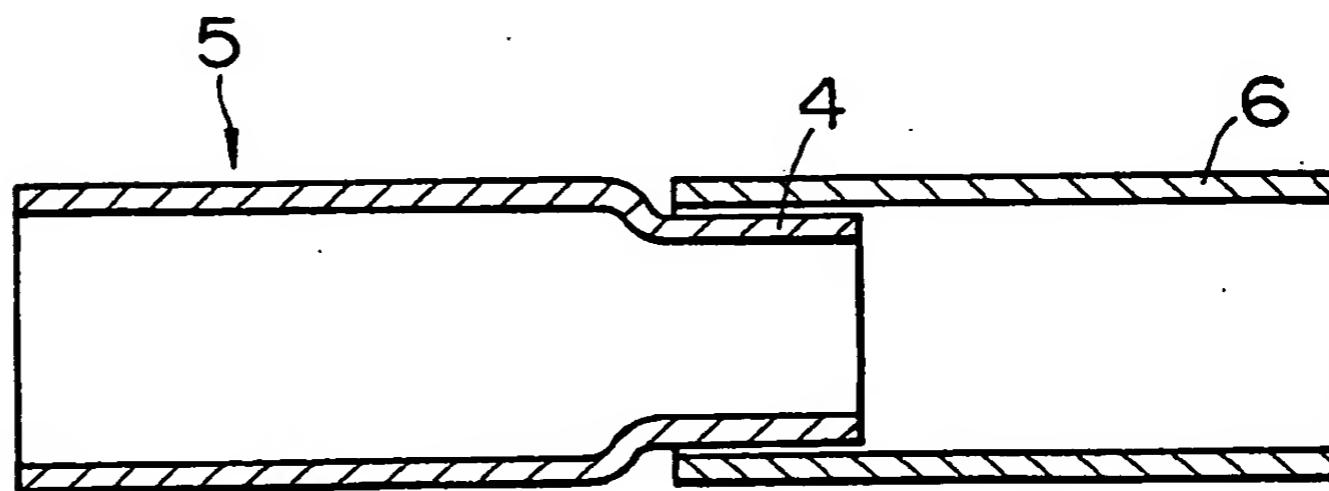


FIG. 2



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㉔ Inventor: Shimizu Makoto Nagoya Technical

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### ㉗ Shape memory hollow body and method of working the same.

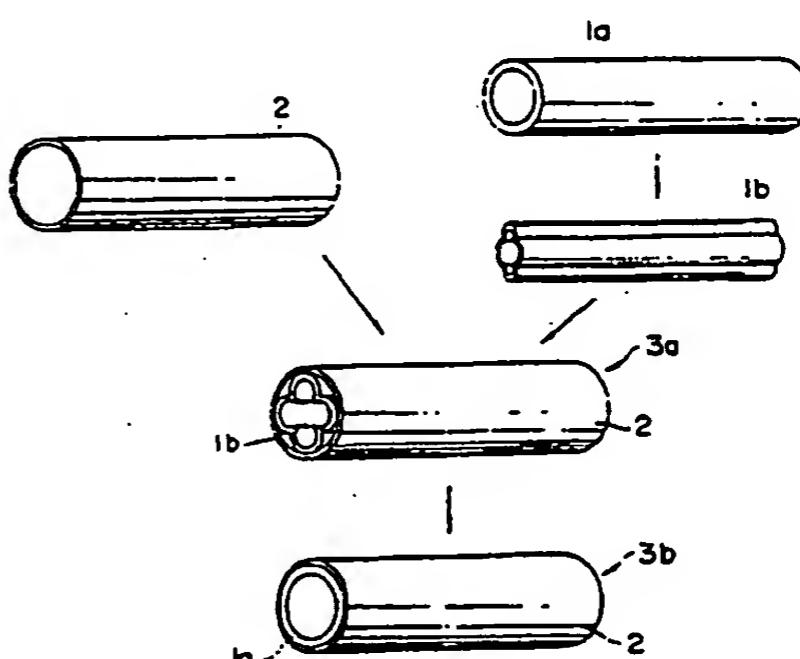
㉗ A shape memory hollow body which is molded from a polyurethane elastomer produced by prepolymer process from a raw material composed of a difunctional diisocyanate, difunctional polyol, and difunctional chain extender containing active hydrogen in a molar ratio of 2.00-1.10 : 1.00 : 1.00-0.10, said polyurethane elastomer containing NCO groups and OH groups in almost equal amounts at the terminals of the polymer chains and having a glass transition point in the range of -50 to 60 °C and a crystallinity of 3 to 50 wt%, said hollow body remembering its asmolded basic shape but taking on a deformed shape which is given when it is deformed at a temperature higher than the glass transition point of the polymer and lower than the molding temperature and then set when it is cooled in the deformed state to a temperature lower than the glass transition point.

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A method of working the above-mentioned shape memory hollow body (1a) remembering its basic shape, said method prising the steps of deforming the hollow body (1a) at a temperature higher than the glass transition point and lower than the molding temperature and then cooling it in the de-

formed state to a temperature lower than the glass transition point, thereby setting it in the deformed state, combining the deformed hollow body (1b) with another member, (2), and heating the combination (3a) to a temperature higher than the glass transition point, thereby causing it to restore its basic shape and achieving firm bonding of the hollow body (1a) to the member.

FIG. 1





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-3 624 045 (STIVERS) * Column 2, line 62 - column 4, line 75; claim 1 * ---	1-6	B 29 C 71/00 C 08 G 18/10 C 08 G 18/32
A	FR-A-1 549 412 (RAYCHEM) * Page 2, right-hand column, line 8 - page 4, left-hand column, line 37; claims 1-4 * ---	1-6	
A	FR-A-1 534 052 (DUNLOP) ---	1-6	
A	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 163 (C-424)[2610], 26th May 1987; & JP-A-61 293 214 (MITSUBISHI) * Abstract * ---	1-6	
A	DE-A-1 704 160 (GUTHOFFNUNGSHÜTTE) -----	1-6	
			TECHNICAL SEARCHED
			B 29 C C 08 G
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	21-08-1990	BOURGONJE A. F.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
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P : intermediate document	& : member of the same patent family, corresponding document		